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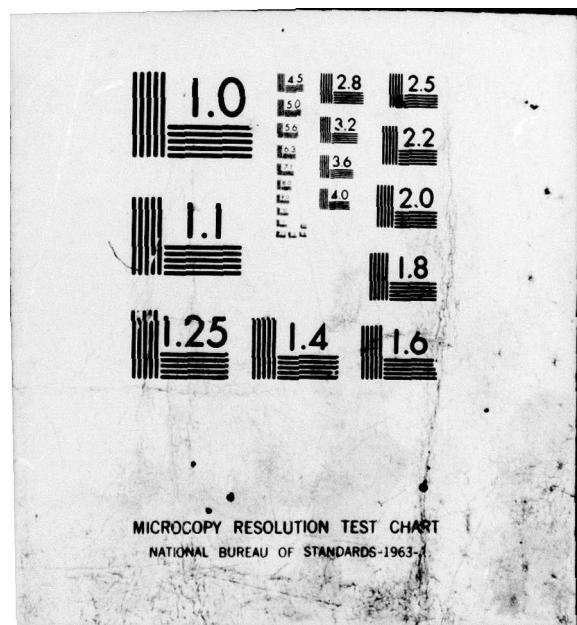
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DETERMINATION OF DISSOLVED NITROGEN AND OXYGEN IN WATER BY HEADSPACE GAS CHROMATOGRAPHY.

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Daniel C. Leggett

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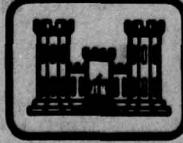
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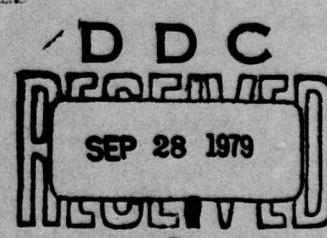


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Measurements of the dissolved gas status of streams and impoundments are of interest because of the relationship between oversaturation and gas embolism in fish. In this study dissolved oxygen and nitrogen were determined by shaking 20 to 25 ml of water with an equal amount of helium in a 50-ml gas-tight syringe and injecting 2 ml of the equilibrated headgas into a gas chromatograph. Oxygen and nitrogen were separated on a 5-Å molecular sieve column at ambient temperature and detected with a hot wire detector using atmospheric air for calibration. Advantages of this method over previously reported methods are 1) oxygen and nitrogen are determined in a single analysis, 2) no specifically fabricated stripping apparatus is needed, and 3) analysis can be done in the field with completely portable, battery-operated equipment. Analysis of a sample of laboratory distilled water by the described method gave values		

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20. Abstract (cont'd)

Cont. for O₂ (corrected for argon) and N₂ of 5.74±0.16 ml/l and 10.71±0.36 ml/l respectively. Calculated values for distilled water based on the literature were 5.71 ml/l for O₂ and 10.76 ml/l for N₂. Dissolved oxygen determined by the Winkler method was 5.64 ml/l. Therefore, the method appears to be accurate and reproducible. Several lake O₂ and N₂ profiles were obtained using this technique. The results for dissolved oxygen compared favorably with those obtained using either the Winkler method or the dissolved oxygen membrane probe. Dissolved nitrogen values were between 92% and 97% of saturation relative to surface water.

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PREFACE

This report was prepared by Daniel C. Leggett, Research Chemist, of the Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this research was provided by the U.S. Army Waterways Experiment Station under Interagency Order No. WESRF 78-120.

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DETERMINATION OF DISSOLVED NITROGEN AND OXYGEN IN WATER BY HEADSPACE GAS CHROMATOGRAPHY

Daniel C. Leggett

INTRODUCTION

Increasing interest in the dissolved oxygen and nitrogen status of lakes and rivers has created a need for simple portable equipment for performing the analysis. In particular, concern over nitrogen "oversaturation" in relation to the problem of gas embolism in fish has created a need for dissolved nitrogen analysis in lakes and streams. Dissolved oxygen has frequently been measured and a number of techniques for field analysis have been developed. However, dissolved nitrogen has infrequently been measured, partly because of the lack of suitable field methods. Gas chromatography is the logical approach since portable instruments are available and the separation of oxygen from nitrogen on molecular sieves has long been used for this analysis. Five basic methods have been used for dissolved gas analysis by gas chromatography: 1) direct aqueous injection, 2) dynamic gas stripping, 3) static gas stripping, 4) static headspace analysis, and 5) multiple phase equilibration or discontinuous gas stripping.

Direct aqueous injection (method 1) is seldom used because it generally lacks sensitivity and chromatographers generally prefer to avoid injecting water. There have been exceptions, however (Hall 1978). The other four methods all involve transferring the components of interest to the gas phase by dilution with another gas. A large increase in sensitivity can be realized in this way because much larger gas than liquid volumes can be safely injected.

Dynamic gas stripping (method 2) involves continuous flow of both water and gas phases. The success of this method depends on a high gas/liquid flow ratio, in which case some sacrifice in sensitivity occurs, or on very efficient transfer of the dissolved components to the gas phase. Several types of devices have been fabricated for this purpose (Williams and Miller 1962, Walker and France 1969, Murray et al. 1975). Some

difficulties in maintaining and accurately measuring the relative water and gas flow rates have been encountered by this investigator and others (Walker and France 1969, Jenkins 1975).

Stripping a fixed volume of liquid with gas (method 3) is the most widely used (Swinnerton et al. 1962a and 1962b). Since it is usually combined with on-column or off-column trapping of the volatiles prior to gas chromatography, there is no need for highly efficient stripping as the sample can be purged for longer periods of time. In this mode it has been used mainly to analyze waters for less easily stripped organic compounds (Novak et al. 1973, Bellar and Lichtenberg 1974) and inorganic compounds (Cohen 1977).

Static headspace analysis (method 4) curiously has also been used mainly for organics (Bassette et al. 1962, Corwin 1969), usually by addition of a salt to increase the gas/liquid partition coefficient. This report will show its applicability to routine dissolved gas measurements using very simple apparatus and portable equipment. A simple and ingenious technique for conducting head space analysis (McAuliffe 1971) involves using a gas-tight syringe for the equilibrating vessel, which also facilitates transfer to the gas chromatograph.

The method of multiple equilibration with a gas by this technique (method 5) has been used by McAuliffe (1971) to determine light hydrocarbons in waters and recently for halocarbons resulting from water chlorination (Leggett unpublished data). In this method, also called discontinuous gas extraction (Kolb 1976), the gas/liquid partition coefficient need not be known or determined *a priori* as it results from the graphical analysis of gas phase concentration vs equilibration number. Thus it is particularly applicable to determination of volatiles in an unknown or difficult matrix where the partition coefficient is unknown, such as in solid materials (Kolb 1976, Kolb and Pospisil 1977). Rasmussen et al. (1976) recently used McAuliffe's

method for determining nitrous oxide and halocarbons in seawater. The method to be reported here was a static headspace analysis (method 4) calibrated by multiple equilibration (method 5) and carried out by McAuliffe's syringe equilibration technique. A similar technique was used by Stanton (1973) to determine inorganic carbon in water and sediments after release of CO₂ by acidification.

METHODS

The method of headspace equilibration was similar to that used by McAuliffe (1971) except that only one equilibration was normally used. The recovery in a single equilibration was determined initially by multiple equilibration, and subsequently a correction factor was applied to the data to save time. Recoveries using a 1:1 volume ratio of He to water were 98.6% for N₂ and 97.2% for O₂+Ar. Water was introduced into a 50-ml gas-tight syringe (Hamilton) by decantation without agitation from the collection vessel, completely filling the syringe barrel. The plunger was then inserted into the end of the barrel with care not to trap air bubbles and the syringe inverted. The needle was removed and any residual air expelled. Then water was expelled until 20 ml remained in the calibrated syringe barrel. The needle was replaced and the air displaced from it with water. Helium was then introduced through the needle by inserting it into a flowing source of gas under slight positive pressure; this was conveniently done using a spare injection port of another gas chromatograph (g.c.). (If a g.c. is unavailable, a tank of He attached to a flow restrictor, again most conveniently a g.c. column, through a short length of tubing containing a tee with a rubber septum port can be used.) Normally an equal volume of gas was introduced, but in any case the exact volumes (to the nearest 0.5 ml) of liquid and gas phases were determined from the graduation on the syringe barrel.

Equilibration was accomplished by vigorous manual shaking for 3 min. During this process, entry of air was avoided because some water entered the syringe needle, forming a vapor seal so that capping the syringe was not found to be necessary. At the end of 3 min, the small amount of water in the syringe needle was expelled, and maintaining positive pressure, the needle was quickly inserted into a septum port attached by means of a short piece of bent tubing to the gas sampling loop on the g.c. About 15 ml of the headgas was forced through the 2 ml loop, and the sample was injected immediately into the g.c. The syringe needle was bent in order to facilitate this operation.

Gas chromatography was performed on a Analytical Instrument Development Model 511 g.c. equipped with a dual hot wire detector. The gases were separated on a 6-ft column of 80-100 mesh Linde 5-Å molecular sieve at ambient temperature, which separated oxygen and argon from nitrogen while oxygen and argon eluted together. Gases were detected by thermal conductivity and the signals were recorded on a strip chart recorder—a portable, battery-powered recorder supplied by Esterline-Angus. Peak areas were used in all calculations and these usually were determined by manual triangulation.

Calibration of the detector was achieved by injection of 100- μ l quantities of atmospheric air (at known temperature, pressure, and relative humidity) via the normal injection port on the g.c. Preliminary injection of different quantities of air established that the detector response was linear over the range of interest. Therefore single point calibration was subsequently used. Concentrations of O₂+Ar and N₂ in sample waters were calculated by application of the ideal gas law using the standard atmospheric ratios of 78.08, 20.95 and 0.93% by volume (exclusive of H₂O vapor) for N₂, O₂, and Ar, respectively (Riley and Skirrow 1975). For the purpose of calibration, Ar was assumed to have the same molar response factor in the g.c. as O₂, even though its thermal conductivity is lower than that of O₂. The error introduced by this assumption is negligible compared to the overall precision of the method and is partly canceled by the presence of approximately the same percentage of Ar both in the calibrating gas and in the dissolved gas phase (0.9 vs 1.7%). The contribution of Ar to the dissolved O₂+Ar peak in sample waters was determined by assuming that the Ar/N₂ ratio was approximately 0.025:1 by volume (Craig et al. 1967, Benson and Parker 1961), or for water known to be saturated with air, tabulated values were used (Riley and Skirrow 1975).

RESULTS AND DISCUSSION

Table 1 shows the results of repeated analysis of a batch of well-aerated laboratory distilled water used for biological oxygen demand determinations. Precision was good, considering that the gas and water volumes were measured with an accuracy of only 0.5 ml (2.5% rel.). Thus, this factor could account for essentially all of the error in this method. In terms of actual concentrations, the standard deviations were 0.16 and 0.36 ml/l for O₂ and N₂ respectively. The precision in replicating standard injections appeared to be slightly better as shown in Table 2, as would be expected since less manipulation is involved. The overall accuracy of this particular set of data was determined by comparison

Table 1. Analysis of distilled water by proposed method.

Replicate	O ₂ conc. (mm ² chart)	N ₂ conc. (mm ² chart)
1	246	425
2	235	441
3	232	456
4	242	451
5	230	411
6	230	448
7	242	445
Average	237	440
Standard deviation	6.6 or 2.8% rel.	14.7 or 3.3% rel.

Table 2. Reproducibility of calibration by air injection.

Replicate	O ₂ response (mm ² chart)	N ₂ response (mm ² chart)
1	200	737
2	202	735
3	203	725

Table 3. Solubility of O₂ and N₂ in water from air at 28°C, 0% R.H.

Source	O ₂ conc. ml/l (STP)	N ₂ conc. ml/l (STP)
g.c. (this work)	5.74	10.71
Winkler (this work)	5.64	—
A.P.H.A. (1971)	5.76	—
Douglas (1964)	—	10.63
Chemical Rubber Co. (1962)	5.68	10.91
Riley and Skirrow (1975)	5.68	10.81
Klots and Benson (1963)	5.86	10.83
Weiss (1970)	5.59	10.64

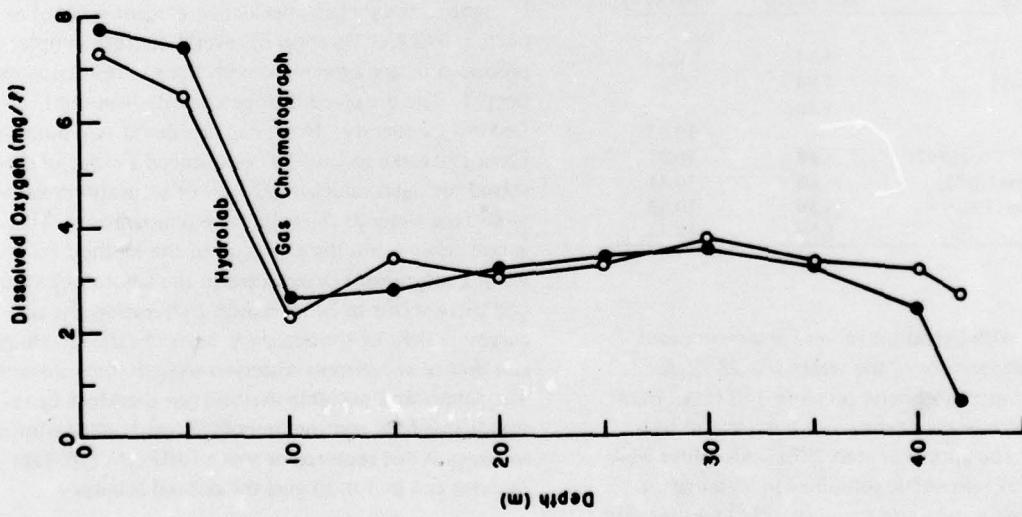
of the average with literature values for air-saturated water. The temperature of the water was 28°C, the air 29°C, and the atmospheric pressure 748 mm. Relative humidity was inadvertently not determined but was assumed to be approximately 50%. All values were corrected to the volumetric solubility in water of air at standard temperature and pressure (STP) and 0% relative humidity. Dissolved oxygen in this same water was also determined by the Winkler method. This value is reported in Table 3 along with representative values from the literature. It is obvious that the values obtained by this method compare favorably with accepted values for air-saturated water at this temperature

and fall within the range of several independent determinations. (The average literature values are 5.71 and 10.76 ml/l STP.) Therefore the method appears to be unbiased and useful for accurate work. The precision of the method (s.d. = ± 0.16 and 0.36 ml/l) can be explained by the precision of liquid and gas volume measurements (± 0.5 ml). Other major sources of error are expected to be temperature fluctuation and manual data reduction, although they did not appear significant in this case. Refinements to be made include improved thermostating of the samples and calibrating gas and electronic integration of the analog signal. It should be possible to use an air-saturated water bath with a thermostat as the calibrating source instead of air. This would be particularly advantageous in the field where air temperature fluctuation could present a standardization problem.

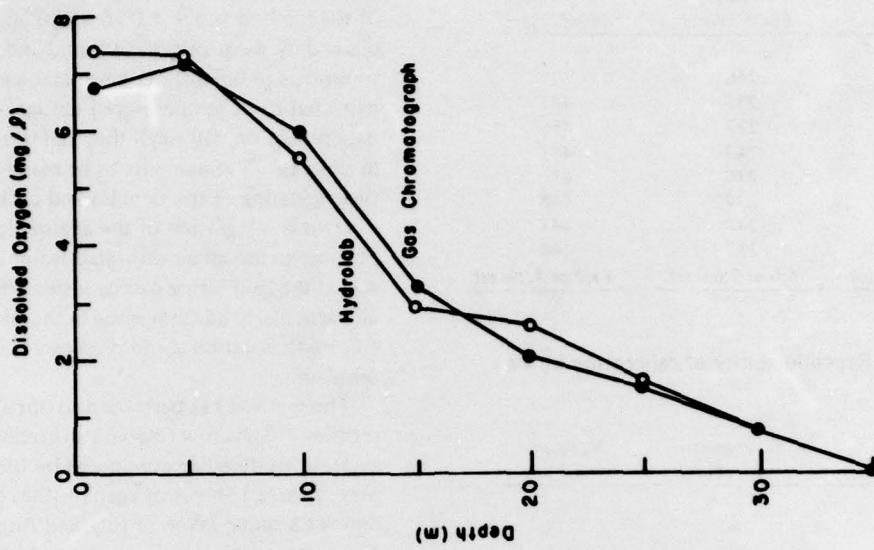
The method has been used to obtain dissolved gas profiles in a shallow reservoir in conjunction with a re-aeration study being conducted by the Corps of Engineers. Figure 1 shows oxygen profiles of Clark Hill Lake, South Carolina, taken in July and August 1977. Gas chromatographic results are for a single analysis of samples collected from depth with a van Dorn sampler and analyzed immediately on board a small boat. Companion measurements made with a Winkler-calibrated dissolved oxygen probe (Hydrolab) are shown mainly to document the agreement between the two techniques. Since the Hydrolab measurements were made in situ and the g.c. measurements were made on discrete samples brought to the surface, perfect agreement was not expected. Winkler titration of several discrete samples produced better agreement with the g.c. results, as expected. The dissolved nitrogen profiles were not verified independently. However, profiles at two points in Clark Hill Lake in July 1977 produced a range of dissolved nitrogen values of 92-97% of saturation relative to surface water at the respective temperature. This is certainly within the precision of the method (assuming saturation) determined in the laboratory study, and there seems to be no reason to question the accuracy in light of the accuracy shown in the lab study and that of concurrent dissolved oxygen measurements. The simple and portable method can therefore be recommended for routine limnologic work when utmost accuracy is not required or when sufficient replicate analyses can be run to give the desired accuracy.

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a. Buoy 10, July 1977.



b. Buoy 15, August 1977.

Figure 1. Dissolved oxygen profiles in Clark Hill Lake, South Carolina—comparison of g.c. and Hydrolab results.

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